

INVESTIGATION OF ELECTROCALORIC EFFECTS IN FERROELECTRIC SUBSTANCES

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DEFINITION OF TERMS AND SYMBOLS

Rationalized MKS units are used throughout. Thermodynamic formulas such as $dU = TdS + Xdx + EdP$ are written for a unit volume of material. This procedure is not exactly proper because the thermodynamic system (the experimental crystal) changes its volume slightly, but only inappreciable errors result.

C = Curie constant. Curie-Weiss Law is $\chi = C/(T - T_p)$.

c_E = Specific heat at constant field (and zero stress).

c_p = Specific heat at constant polarization (and zero stress).

D = Electric displacement. $D = \epsilon_0 E + P$.

E = Applied electric field.

G_1 = Elastic Gibbs function. $G_1 = U - TS - xX$.

$G_{10} = G_1$ at some (arbitrary) reference temperature.

p = Electric dipole moment.

P = Electric polarization per volume. P_s is the spontaneous electric polarization per volume.

p^E = Pyroelectric coefficient at constant field (and stress).

S = Entropy per volume.

T = Temperature in degrees Kelvin.

T_c = Critical temperature (loosely speaking, either T_f or T_p).

T_f = Ferroelectric Curie temperature = the temperature at which P_s disappears when the substance is heated.

T_p = Paraelectric Curie temperature as defined by the Curie-Weiss Law,

$$\chi = C/(T - T_p).$$

U = Internal energy per volume.

X = Applied stress. (Tensile stress has a positive sign.)

x = Strain. (Elongation has a positive sign.)

ϵ_0 = Electric permittivity of vacuum = 8.85×10^{-12} coul²/n·m².

ζ = Devonshire's sixth-order coefficient (of P^6) in G-expansion.

ξ = Devonshire's fourth-order coefficient (of P^4) in G-expansion. (ψ appears as a misprint in place of ξ in Eq. 7 and 9 of Status Report No. 1.)

ρ = Mass density.

χ = Electric susceptibility. $dP = \epsilon_0 \chi dE$. The symbol χ may carry subscripts such as p (paraelectric), or superscripts such as T (constant temperature), X (constant stress), etc.

ψ = The non-linear polarization function in the Devonshire expansion.
Usually written $\psi(P)$.

ψ' = The derivative of $\psi(P)$ with respect to P . Usually written $\psi'(P)$.

ω = Devonshire's second-order coefficient (of P^2) in G-expansion.

Note: Equations in the two Status Reports are numbered in order beginning with those in Status Report No. 1.

SUMMARY OF PREVIOUS STATUS REPORTS 1, 2, 3, & 4

Status Report No. 1 contained a thermodynamic description of the electrocaloric effect, the pyroelectric effect, and the relationship between them.¹ It was shown that the same crystalline properties give rise to both effects and that the relevant thermodynamic coefficients can be determined from electrocaloric measurements. So-called "tertiary effects" which arise from inhomogeneous temperatures or fields can be so large that to mask the "real" effects; the tertiary effects are more easily eliminated in the electrocaloric than in the pyroelectric measurements.

The apparatus and techniques that were devised for accurately regulating the temperature of the experimental chamber and making simultaneous measurements of the changes in electric polarization and temperature that occur with changes in applied field were described.

Status Report No. 2 included an account of the measurements of the electrocaloric effect in KH_2PO_4 over the temperature range from 78°K to 136°K. Numerical values for the pyroelectric coefficient and its variation with temperature were determined from the measured electrocaloric effect. Reliable values for the Devonshire coefficients could not be determined from the electrocaloric effect because their determination depends upon measured values of changes in polarization, and the polarization of KH_2PO_4 is nearly saturated in the nearly-reversible tail of the hysteresis loops where the electrocaloric measurements are valid. (E.g., see Fig. 4 of Status Report No. 2.)

Report No. 3 describes the changes made in the apparatus and techniques that permitted electrocaloric measurements of $\Delta T/\Delta P$ in the nearly-reversible tails of the hysteresis loops (i.e., in the "saturation" region). These were the use of (1) a well-regulated, high-voltage d-c power supply, (2) a much more sensitive d-c amplifier with a much higher input resistance for measurements of polarization, and (3) a charge-biasing procedure to suppress the zero of the charge-measuring equipment.

The degree of reversibility of the electrocaloric effect in the tails of the hysteresis loops for potassium dihydrogen phosphate was observed, and electrocaloric measurements of both $\Delta T/\Delta P$ and $\Delta T/\Delta E$ were made of this substance over the entire temperature range for which the electrocaloric effect is appreciable (77°K to 136°K). Maximum sensitivity for low-impedance pyroelectric detectors used in the ferroelectric state is not obtained until the

applied biasing field is sufficiently large to bring the specimen into the nearly-reversible tail of the hysteresis loop. When operated in the paraelectric state, the pyroelectric coefficient can be controlled at will by a suitable biasing field, the sensitivity increasing with the field.

A relatively simple expression was found which gave a good fit to measured values of $(\Delta T/\Delta P)_S$ over the entire temperature range right through the Curie temperature. It is

$$(\partial E/\partial P)_T = (\rho c_p/T)(\Delta T/\Delta P)_S = 3.63 \times 10^7 P - 4.80 \times 10^{12} P^5.$$

However, we did not succeed in finding a Gibbs function G_1 that accurately describes both the ferroelectric behavior and the pyroelectric coefficient over the entire range of temperature.

The variation with temperature and field of an inner field coefficient γ that can be used to describe the spontaneous polarization and the electrocaloric effect was determined.

A computer program using Fortran IV was written for an IBM 7040 computer; its use vastly increased the speed and accuracy of some of the tedious computations and curve-plotting.

Status Report No. 4 is an account of the electrocaloric effect in triglycine sulfate, $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ throughout the temperature range over which an appreciable effect exists, 273°K to 334°K, and at electric fields up to 306 kv/m.

This material has a large pyroelectric coefficient especially near the Curie temperature (322.6°K or 49.45°C) as expected. The first Devonshire

coefficient ω is a continuous function of temperature with no change in slope right through the Curie temperature, a behavior to be expected of a second-order ferroelectric transition. Because of the relatively high temperature at which the electrocaloric effect occurs in this substance, relaxation polarization and/or ohmic conductivity effects are so large that they prevent an accurate determination of the second Devonshire coefficient ξ .

The pyroelectric coefficient was determined from the electrocaloric measurements. It is a strong function of temperature. It is nearly independent of field below the Curie temperature, but it can be controlled by adjusting the field above the Curie temperature.

LIST OF EQUATIONS

A list of the most important equations from previous reports is given below. Equations are numbered consecutively, beginning with the first report.

$$dU = TdS + Xdx + EdP \quad (1)$$

$$dT = (T/\rho c_p)(\partial E/\partial T)_p dP \quad (2)$$

$$dT = (T/\rho c_E)(\partial P/\partial T)_E dE \quad (4)$$

$$P = f(a) = f[p(E + \gamma P)/kT] \quad (5)$$

$$dT = (\gamma/\rho c_p)PdP \quad (6)$$

$$dG_1 = -SdT - xdx + EdP \quad (7)$$

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 \quad (8)$$

$$(\partial G_1/\partial P)_T = E = \omega(T)P + \xi P^3 + \zeta P^5 \quad (9)$$

$$dP = p^{X,E} dT \quad \text{where } p^{X,E}(\partial P/\partial T)_{X,E} \quad (20)$$

EXPERIMENTAL PROCEDURE

Instrumentation

A new instrument, a Keithley Model 148 Nanovolt Null Detector, was obtained to measure the small electrocaloric temperature changes. This instrument has a greater immunity from stray pick-up and a better signal-to-noise ratio for large deflections than the instrument previously used.¹ Because of its high input resistance, this instrument also serves as a null detector for the potentiometer that is employed to measure the temperature of the experimental chamber.¹

KDA Sample

The potassium dihydrogen arsenate (KH_2AsO_4) sample (hereafter called KDA) was a single crystal obtained from the Clevite Corporation. Its major faces were oriented perpendicular to the ferroelectric (c) axis and were coated with air-dried silver paste. A copper-constantan thermocouple was mounted on but electrically insulated from the lower electrode, and the entire specimen was suspended in the chamber as described in previous reports.^{1,2} Some important properties of this specimen are tabulated below:

Area of major surfaces	0.868 cm ²
Thickness	2.65 mm
Crystal structure ⁵	Tetragonal
Ferroelectric axis ⁵	c
Curie Temperature (T_f) ⁵	~96°K

Other properties of KDA have been reported by Bantle⁶, Busch⁷, and by Stephenson and Zettlemoyer⁸. No pyroelectric or electrocaloric studies have been reported for KDA.

Measurements of KDA

Large single crystals of KDA, like KDP, tend to crack when cooled through the Curie temperature and with an electric field applied. This field may evidently be externally applied or be due to the sudden polarization of an open-circuited crystal as it is cooled through the Curie temperature. Consequently, no a-c hysteresis loops were taken on the specimen used for the electrocaloric measurements; careful inspection after the measurements were completed revealed no cracks.

In order to prevent arcing as the higher voltages were applied, the crystal chamber was filled with dry helium at atmospheric pressure. This gas increases the heat leaks to and from the crystal, but the resulting errors were minimized by measuring only the "instantaneous" temperature changes as seen on the strip-chart recorder.

At each temperature, before any readings were taken, the crystal was cycled several times over the range of electric field to be used until reproducible hysteresis cycles were obtained. Then, equal step-wise changes in field were applied at one-minute intervals for at least two complete cycles and simultaneous changes in electric polarization and temperature were recorded on a pair of 11-inch strip-chart recorders.^{1,2} All steps of one of these two cycles were used for the computations.

Subsequent to the traversal of the hysteresis cycles, the charge sensitivity of the apparatus was increased and the positive half cycle of the program was traversed several times to establish reproducibility after which this half-cycle was traversed two more times while data were recorded. The same

routine was then repeated for the negative half cycle. The duration of each step in the positive or negative half cycles was 2 minutes. The purpose of these traversals was to obtain step-wise data in the reversible tails of the hysteresis loops at increased charge sensitivity.

Complete experiments as described above were run at 17 different temperatures distributed over the twenty-degree temperature range for which appreciable electrocaloric effects exist, from 80.45°K to 100.57°K. Five of these were in the paraelectric region. Measurements over the temperature range were not taken in order of increasing or decreasing temperature so that any effects of ageing could be observed. None were observed, in contrast to the behavior of triglycine sulfate.⁴

Each field step applied to KDA produces a sudden change in charge which is followed by a slow "relaxation" charge similar to that observed with potassium dihydrogen phosphate^{2,3} but much smaller. Only those changes that appeared to be practically instantaneous on the strip chart were included in the measured values of polarization. There was a slight indication that a slow temperature change accompanied the slow part of the dielectric polarization, but only the sudden changes were included in the measurements.

The computations were made by putting the values that were read from the strip-chart recorders onto punch cards and programming the IBM 7040 computer to make the calculations and plot the dielectric and electrocaloric effects.

Detection of Latent Heat of Transition

The results of the preceding dielectric and electrocaloric measurements led us to suspect that the ferroelectric transition in KDA was of first order

rather than second order so we ran two cooling curves through the transition temperature in an attempt to discover if the transition was characterized by a latent heat (first-order transition) or by merely a large anomaly in the specific heat (second-order transition). The cooling curves were obtained by placing liquid nitrogen in the dewar in the usual fashion and turning off the heaters. (See Fig. 1 of Status Report No. 1.) After a while, the chamber cooled at a constant rate with the crystal lagging a constant amount behind the chamber. As the crystal cooled, the temperature of the chamber and the temperature-difference between the chamber and the crystal, were recorded. At the same time, an electrometer was connected across the crystal so that the change of polarization (current and time) could be simultaneously recorded. Care was taken that only a negligible potential difference, about 0.01 volt, appeared across the terminals of the crystal so that its bulk was in a field-free condition.

Thermal Depolarization

Preliminary measurements of the pyroelectric effect in TGS and tartaric acid were made by the method of thermal depolarization. These measurements are being continued and will be reported subsequently.

DISCUSSION OF RESULTS

Dielectric and Electrocaloric Effects

KDA was selected for these experiments because of its similarity to KDP.^{6,7} We had found that the electrocaloric effect in KDP is quite unlike that in Rochelle salt.⁹ In particular, we were unable to fit the measured variation of the pyroelectric coefficient of KDP with temperature to a Gibbs function

G_1 that would also describe the ferroelectric behavior. Moreover, the first Devonshire coefficient ω for this substance was not a well-behaved function near the Curie temperature. We hoped that measurements of KDA would either verify or negate the results we obtained with KDP^{2,3} and perhaps throw some light on the drastic difference between the electrocaloric effects in KDP (or KDA) and triglycine sulfate (or Rochelle salt).

Typical dielectric and electrocaloric behaviors of KDA above and below the Curie temperature are displayed in Fig. 1 and Fig. 2. (These curves were hand plotted because it was not feasible to reproduce the original ones plotted by the computer.) These curves exhibit the gross qualitative features that are typical of all of the ferroelectric materials studied: an electrocaloric temperature rise that is quadratic with respect to the applied field if the crystal is in the paraelectric phase (Fig. 1) but which is roughly linear with respect to applied field if the crystal is in the ferroelectric phase and if the field is large enough for approximate reversibility. When low fields are applied with the crystal in the ferroelectric phase, the results mean little because of irreversible heating and the existence of irregular structure and orientation of the ferroelectric domains.

Most of the results that follow are based on measurements such as those illustrated in Figs. 1 and 2 that were made at a number of different temperatures.

The lowest of the three curves of Fig. 3 represents the remanant polarization, the value at $E = 0$, as read from the step-wise hysteresis loops (e.g., Fig. 2). The middle curve represents a near-coincidence of three values:

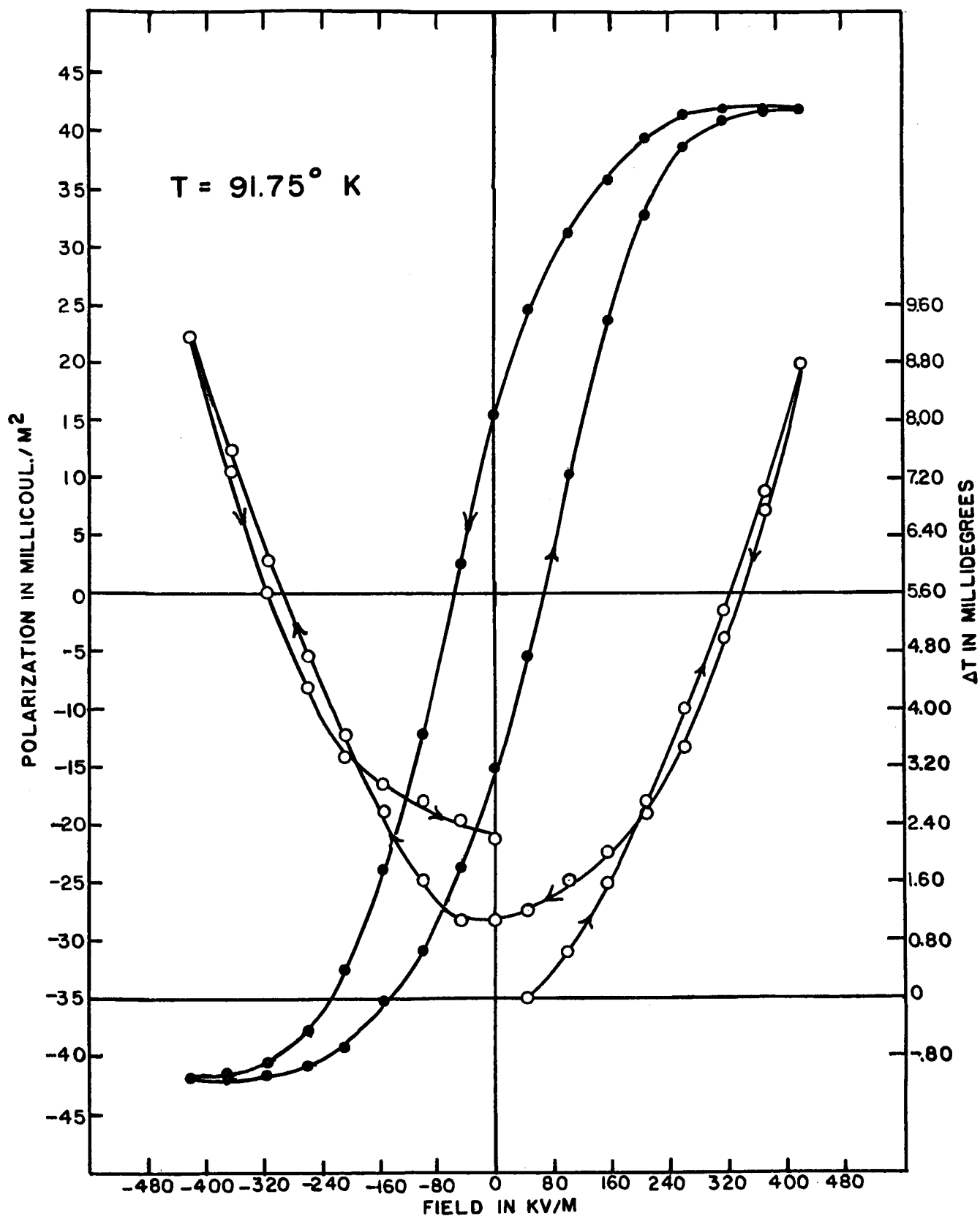


FIG. 1 KDA BELOW THE CURIE TEMPERATURE

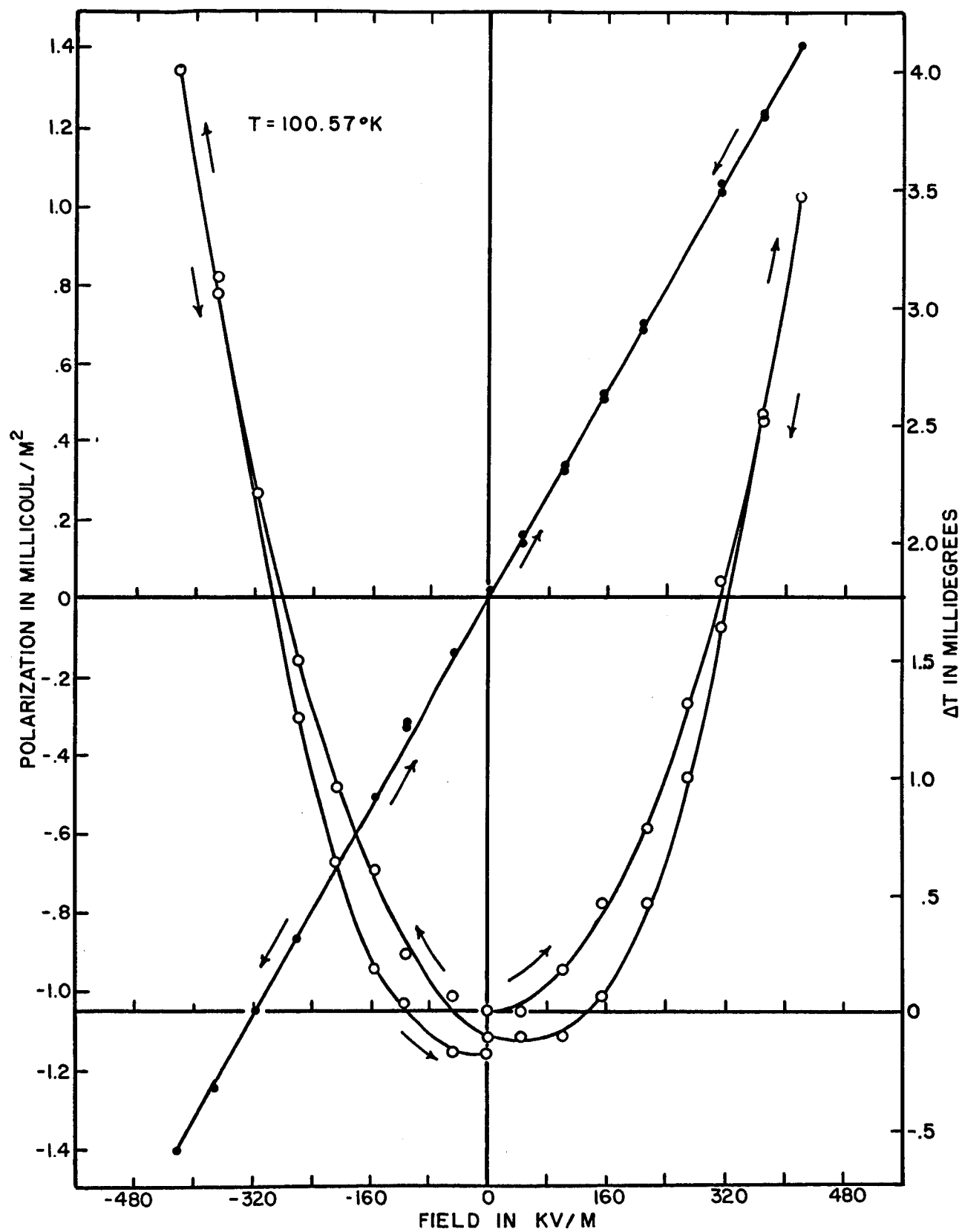


FIG.2 KDA ABOVE THE CURIE TEMPERATURE

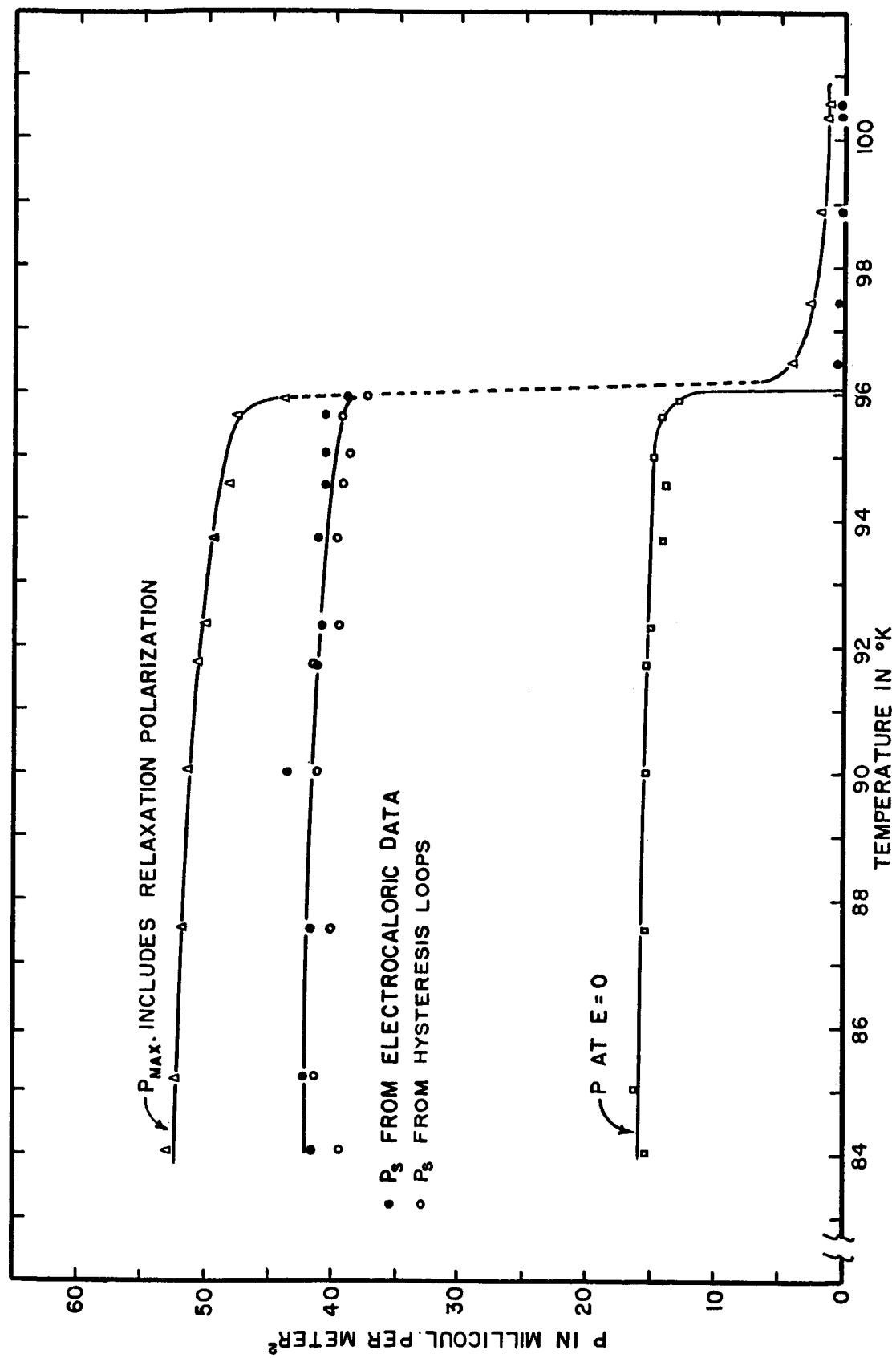


FIG. 3 POLARIZATION OF KDA

(1) the maximum polarization obtained from the hysteresis loops, (2) the spontaneous polarization P_s obtained by extrapolating the tips of the hysteresis loops, and (3) the spontaneous polarization P_s determined from the electrocaloric measurements by extrapolating plots of ΔT vs P^2 to the $\Delta T = 0$ axis.¹ The agreement to within 4% between the values of P_s determined from dielectric and electrocaloric measurements is partly fortuitous because both involve extrapolations of questionable validity. The discrepancy between P_s (middle curve) and $P(E = 0)$ is of course typical of the non-reversible behavior of most ferroelectric substances.

The upper curve gives the values of maximum polarization that would be obtained during the hysteresis cycles if the slow part of the polarization were included in reading the step-wise changes from the strip charts. The slow part is seen to be quite large even at the lower temperatures. Above the Curie temperature, inverse susceptibility of KDA is evidently well-represented by the Curie-Weiss law as shown in Fig. 4,

$$\partial E / \partial P = (T - 94.25) / \epsilon_0 \cdot 2349.$$

Below the Curie temperature, the experimental values are much less consistent because the measurements must be made in the reversible region near the tips of the hysteresis loops where the polarization changes but little with applied field. However, the data show that $(\partial E / \partial P)_s$ does not go to zero at the critical temperature as expected. In fact, the dielectric behavior shown in Fig. 4 is more characteristic of a first-order than a second-order ferroelectric transition. Qualitative features of typical first- and second-order transitions are shown below after Devonshire.¹⁰

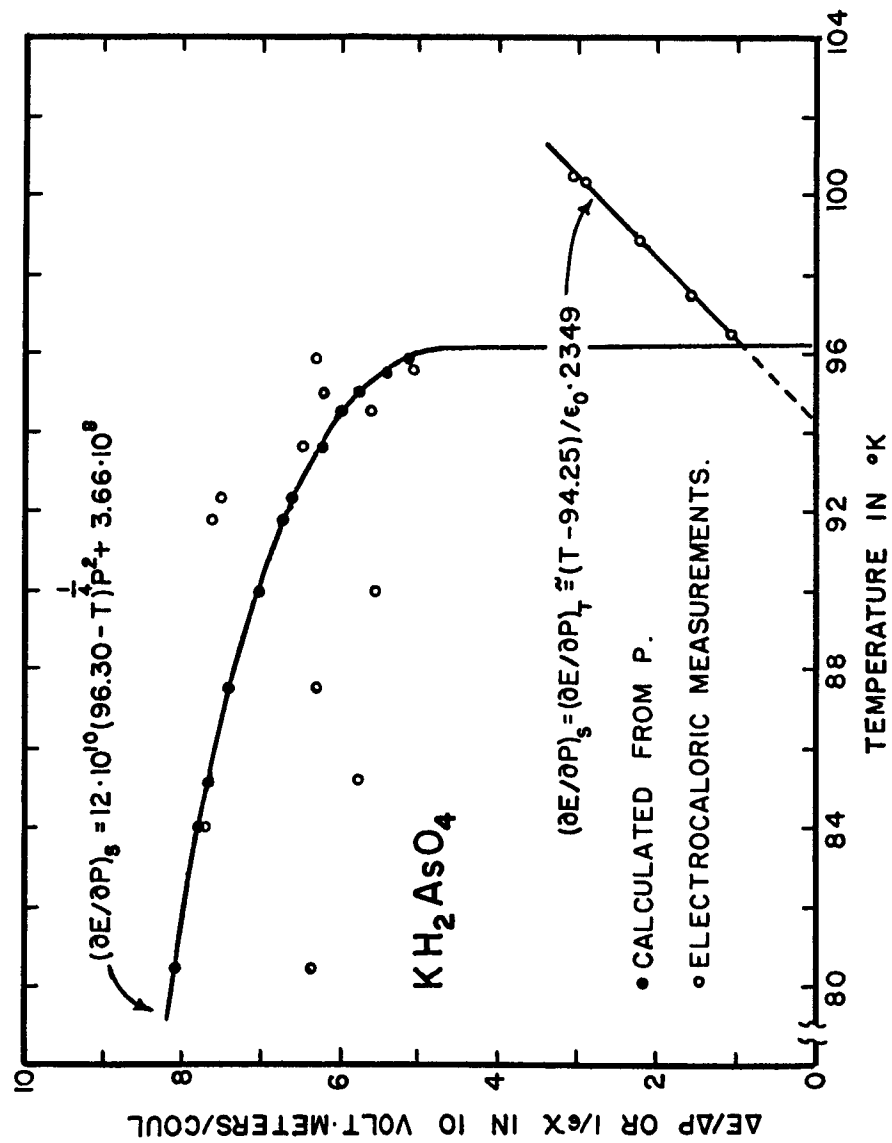


FIG. 4 ANALYTICAL & MEASURED VALUES OF $(\partial E/\partial P)_S$

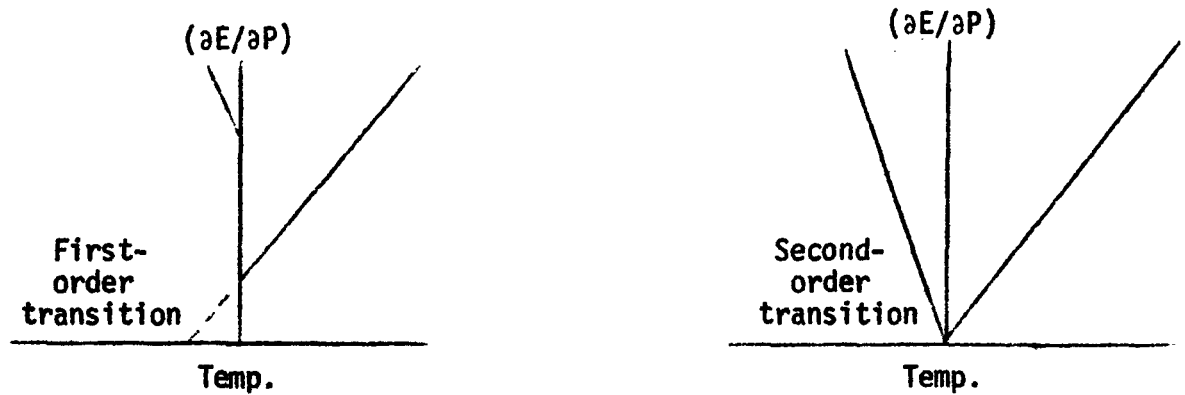


Fig. 5. Prototype First- and Second-Order Ferroelectric Transitions.

The values shown in Fig. 6 were obtained from the simultaneous observation of the electrocaloric temperature changes ΔT and the changes in polarization ΔP that accompanied the step-wise changes in applied field near the tips of the hysteresis loops. Substituting these measured values into Eq. (1)¹ gives

$$(\partial E / \partial T)_P = (\rho C_P / T)(\Delta T / \Delta P)_S,$$

and it is these values of $(\partial E / \partial T)_P$ that are shown in Fig. 6. Above T_C the agreement between the measured values of $\Delta T / \Delta P$ and the value computed from the Curie-Weiss law are in good agreement. This means that an equation of state (Curie-Weiss law) has been found which is consistent with both the dielectric and electrocaloric behavior of KDA. Moreover, this equation of state is derivable from a reasonable expression for the elastic Gibbs function. These relationships are

$$G_1 = G_{10} + P^2/2,$$

and

$$E = (\partial G_1 / \partial P)_T = \omega P,$$

where, for KDP,

$$\omega = (T - 94.25) / \epsilon_0 \cdot 2349.$$

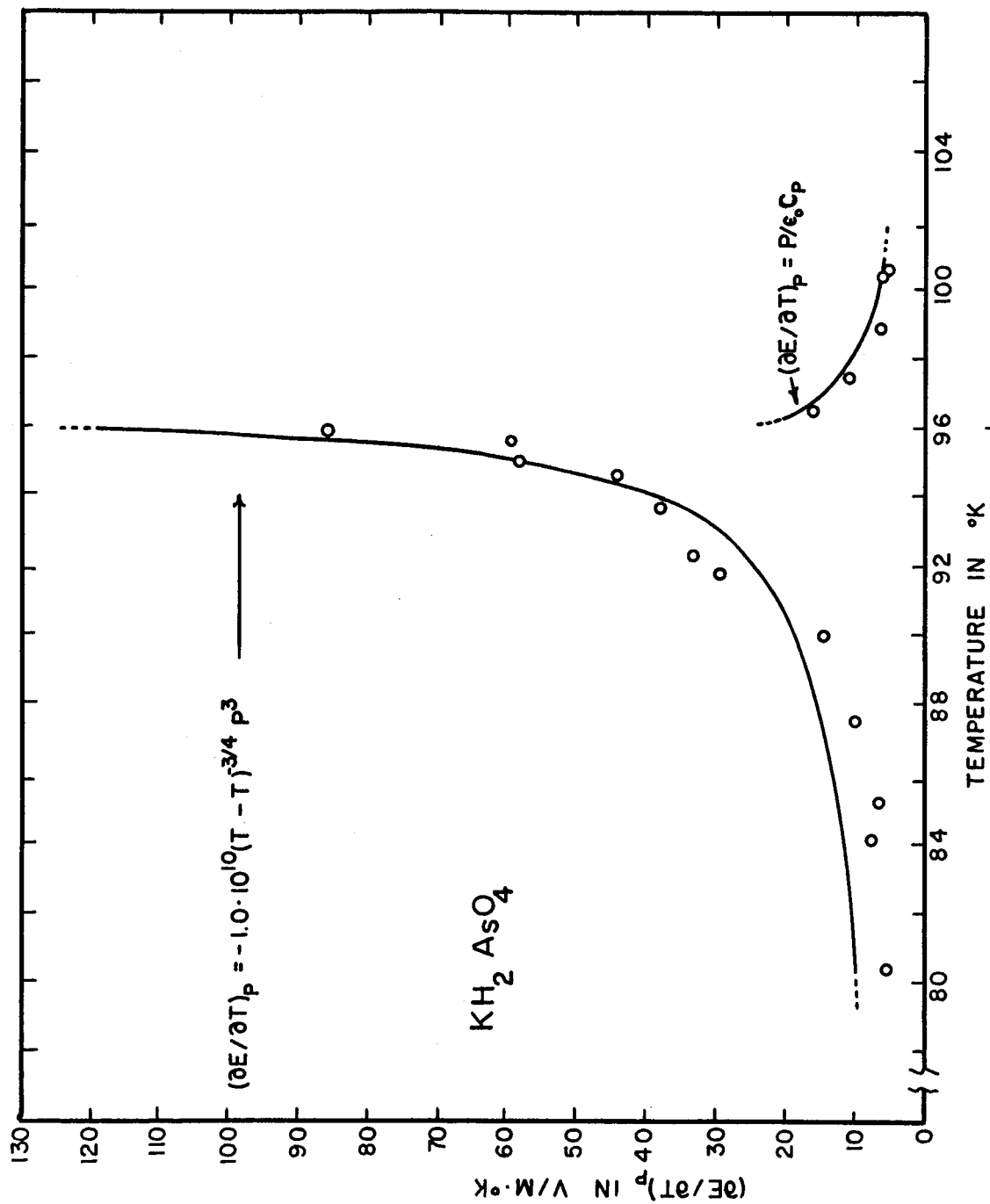


FIG. 6 ANALYTICAL & MEASURED VALUES OF $(\partial E / \partial T)_p$

With experimental values for $(\partial E/\partial T)_P$ below T_C available from the electrocaloric measurements (Fig. 6), one would expect to be able to obtain an equation of state by integration. Unfortunately, electrocaloric measurements cannot be made for arbitrarily selected values of P ; e.g., below the Curie temperature, values of P less than P_S are not experimentally accessible, and values of P at low values of E are not thermodynamically reversible.

Because of this limitation, a number of expressions were tried as a fit to the values displayed in Figs. 4 and 6, expressions suggested by a reasonable form of the elastic Gibbs function

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 \quad (8)$$

or
$$(\partial G_1/\partial P)_T = E = \omega P + \xi P^3 + \zeta P^5 \quad (9)$$

where ω and perhaps ξ and ζ are temperature dependent. Above the Curie temperature, a suitable fit is the Curie-Weiss expression previously cited, the higher-order terms being negligible for the small values of P obtained. The agreement between the values of $(\partial E/\partial T)_P$ obtained from the Curie-Weiss law and from the electrocaloric measurements is evident in Fig. 6 (in the region above T_C).

It is ordinarily believed that ω is continuous function of T right on through the Curie temperature and into the ferroelectric region¹¹; however, we were not able to find a reasonable expansion of the elastic Gibbs function which contained a Curie-Weiss term ω below the Curie temperature. By omitting the Curie-Weiss term below T_C , an analytical expression was found which fits the experimental values fairly accurately. It is

$$G_1 = G_{10} + 3.66 \times 10^8 P^2/2 - 4.00 \times 10^{10} (T_C - T)^{1/4} P^4/4, \quad (32)$$

$$\text{then } E = (\partial G_1 / \partial P)_T = 3.66 \times 10^8 P - 4.00 \times 10^{10} (T_C - T)^{1/4} P^3, \quad (33)$$

$$1/\epsilon_0 \chi_T = (\partial E / \partial P)_T = 3.66 \times 10^8 - 12.0 \times 10^{10} (T_C - T)^{1/4} P^2 \quad (34)$$

$$\text{and } (\partial E / \partial T)_P = 1.00 \times 10^{10} P^3 / (T_C - T)^{3/4}. \quad (35)$$

Thus as T approaches T_C , $(\partial E / \partial P)_T$ approaches 3.66×10^8 , and $(\partial E / \partial T)_P$ approaches infinity. These expressions are represented (below T_C) by the solid lines in Figs. 4 and 6. Experimental values of polarization at maximum field (i.e., in the reversible region) were used in computing these curves.

The above expression, Eq. (33), correctly predicts a polarization catastrophe at $T = T_C$ although, as most analytical expressions do, it overdoes the matter by predicting that the spontaneous polarization becomes infinite at the Curie temperature; i.e., at $E = 0$,

$$P_s = 9.15 \times 10^{-3} / (T_C - T)^{1/4}.$$

The calculated electrocaloric values predicted from these equations differ by no more than 18% from the experimental values.

If the Curie-Weiss law is applicable, the "dP" form of the electrocaloric equation, Eq. (2), reduces to²

$$1/\epsilon_0 C = (2\rho C_p / T)(\Delta T / \Delta P^2) \quad (26)$$

$$\text{or } \Delta T = (T / 2\epsilon_0 C \rho C_p) \Delta P^2.$$

Consequently, a plot of the electrocaloric temperature change ΔT vs $\Delta(P^2)$ should be a straight line which passes through the origin and has a slope

given by the factor $(T/2\epsilon_0 C_p c_p)$. An example of such a plot of experimental values for a temperature barely above T_c is shown in Fig. 7. Using the values of specific heat measured by Stephenson and Zettlemoyer,⁸ we determined the Curie constant from each of the temperatures above T_c at which measurements were made.

<u>Temperature</u>	<u>C from ΔT vs ΔP^2</u>
96.50°K	3090
97.45°K	2948
98.90°K	3040
100.39°K	2950
100.57°K	3070
Mean Value	3019

Our step-by-step dielectric measurements yield a value for C of 2350; Busch, from a plot of the Curie-Weiss relationship, obtains a value of 2600. Evidently the values for the Curie constant that are obtained from the electrocaloric data are somewhat too large.

The Order of the Transition in KDA

The distinction between first- and second-order transitions is simple enough in principle. Not only is a first-order ferroelectric transition characterized by a latent heat whereas a second-order transition is characterized by a discontinuity in specific heat (and no latent heat), but a first-order transition is accompanied by a discontinuity in both spontaneous polarization and reciprocal susceptibility. In practice, the distinction is often difficult; the latent heat may be small and confused by thermal hysteresis of the transition temperature, and the discontinuities in spontaneous polarization

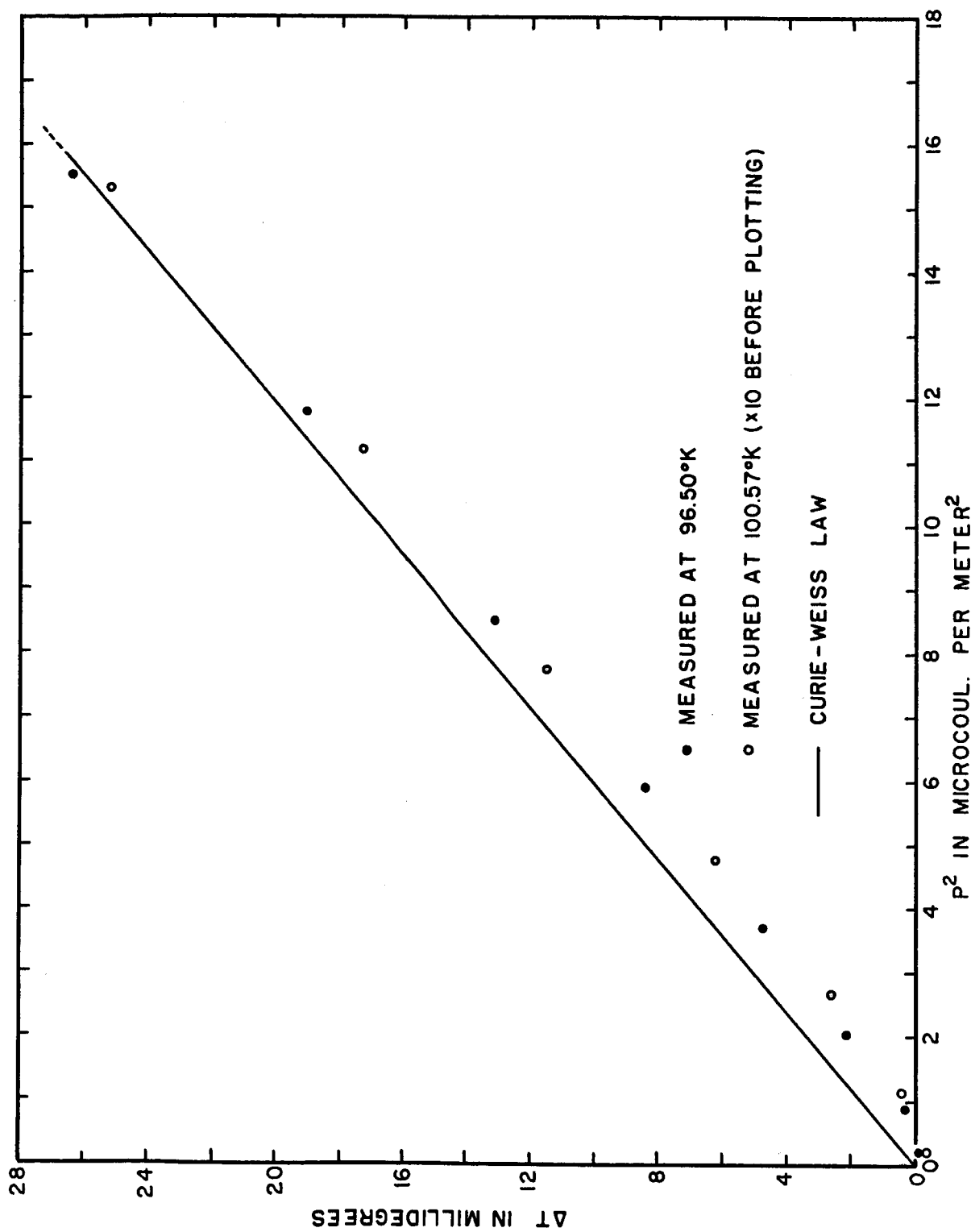


FIG. 7 THE CURIE-WEISS LAW FOR KDA

or susceptibility may be reduced to a negligible values by the finite measuring field. Moreover, the transition may be spread over an appreciable temperature range because of crystalline strains, impurities, or other defects.

Our measurements of KDA -- the spontaneous polarization (Fig. 4), the static reciprocal susceptibility $(\partial E/\partial P)_S$ as determined from the electrocaloric effect, and the anomalous behavior of " ω " as determined from the electrocaloric effect -- all suggest that the ferroelectric transition is of first rather than of second-order. Consequently, we looked for a latent heat of transition by the method of cooling curves as described earlier in this report.

Only enough of such a cooling curve is reproduced in Fig. 8 to display the following features: the constant rate of cooling, except in the transition region, the small "hook" in the cooling curve of the crystal which is reminiscent of the supercooling of a liquid, and the regressions in the behavior of polarization with respect to both time and temperature that appear in the region of the "hook."

The quantity of heat lost by the crystal during the anomalous part of the cooling curve (the transition) was determined from the area under this portion of the curve, the appropriate constants being determined from the observed rate of cooling and the temperature difference between the crystal and its surroundings during the periods of uniform cooling outside the transition region. The quantity of heat lost by the crystal during the transition (96.5°K to 95.2°K on Fig. 8) was about 100 cal/mole. Stephenson and Zettlemoyer have made careful measurements of the specific heat of KDA throughout this temperature range.⁸ Their results differ from ours in three respects:

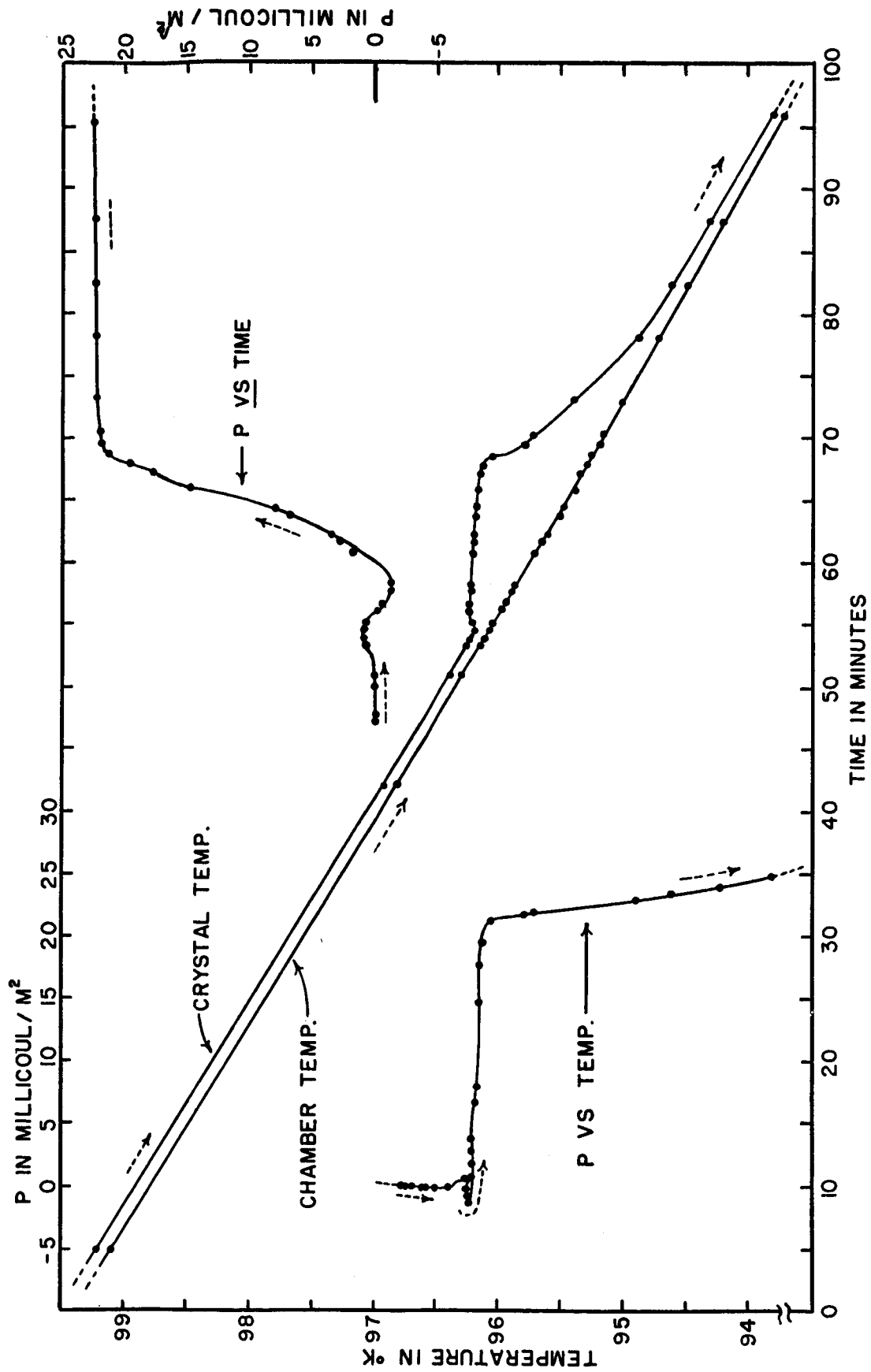


FIG.8 COOLING RATE FOR KDA

they obtain a somewhat smaller value (84 cal/mole) for the heat of transition, they observe that the transition temperature is spread over a range of about 9.2°K where as ours is confined to about 1.3°K, and their cooling curves (a separate experiment from their specific heat measurements) show no evidence of supercooling. We believe that these discrepancies arise because our measurements were made on a short-circuited single crystal whereas theirs were made on granular or powdered material; the formation of domains and the concomitant thermal effects of spontaneous polarization would be inhibited by small, irregularly-shaped specimens and by the lack of field-free conditions in such material. It would seem that reliable measurements of c_E could be made only with large, short-circuited crystals, therefore it would be desirable to repeat the careful measurements of Stephenson and Zettlemoyer under such conditions. The "hook" in our cooling curve and the discrepancy between our results and those of Stephenson and Zettlemoyer tend to confirm the evidence from our static dielectric and electrocaloric measurements that the ferroelectric transition in KDA is of the first order and to verify our results previously obtained with KDP.^{2,3}

The increase in the polarization of the essentially short-circuited crystal as determined by the charge that flowed in the external circuit as the crystal was cooled through the ferroelectric transition is also shown in Fig. 8. Note that the "hook" in the cooling curve is reflected in the behavior of polarization but with some time lag and an extra-large "dip" in the polarization as a function of time. This time shift, the lack of a perfectly discontinuous change in polarization, and the slight slope in the cooling curve during the transition period are all attributed to the fact that the crystal must cool from the outside in. Actually, the changes in polarization as

observed in the recorded electrometer current were abrupt and erratic. Also, it is for this reason that little more than order-of-magnitude accuracy can be assigned to the value of polarization shown; it lies between our previously-measured of saturation polarization and the polarization at $E = 0$.

The Pyroelectric Coefficient

The pyroelectric coefficient p^E is by definition and from Eq. 4 given by

$$p^E = (\partial P / \partial T)_E = -(\rho c_E / T) \Delta T / \Delta E \quad (4')$$

for a measured electrocaloric effect $\Delta T / \Delta E$. In the case of KDA, the pyroelectric coefficient is readily determined from the Curie-Weiss law above T_C . Below T_C the electrocaloric method fails to give values of p^E not because the electrocaloric measurement of $\Delta T / \Delta E$ is invalid but because reliable values of c_E are not available for the reasons stated in the previous paragraphs.

SUMMARY

Studies of the electrocaloric effect in single crystals of potassium dihydrogen arsenate (KDA) were made throughout the temperature range over which the effect is appreciable, from 80.45°K to 100.57°K, which included the ferroelectric transition temperature.

The dielectric and electrocaloric behavior of KDA is similar to that of KDP. The first Devonshire coefficient ω is not a smooth function of T through the transition region, and no analytical expression for the elastic Gibbs function G_1 was found that would describe the crystal both above and below the Curie temperature. The slow part of the change in polarization that

accompanied each step-wise change in applied field was similar to but smaller than those observed with KDP. Both the static dielectric measurements and the electrocaloric measurements taken in the nearly-reversible tails of the hysteresis loops gave evidence for believing that the ferroelectric transition in KDA is of first-order rather than second-order. Cooling curves taken of the single-crystal, short-circuited specimen supported this belief and were at variance with specific heat measurements reported for polycrystalline, open-circuited specimens.

LIST OF REFERENCES

1. G. G. Wiseman et al., "Investigation of Electrocaloric Effects in Ferroelectric Substances," Status Report No. 1, NASA Research Grant NsG-575 with The University of Kansas, March 1, 1964 to August 31, 1964.
2. G. G. Wiseman et al., "Investigation of Electrocaloric Effects in Ferroelectric Substances," Status Report No. 2, NASA Research Grant NsG-575 with The University of Kansas, September 1, 1964 to February 28, 1965.
3. G. G. Wiseman et al., "Investigation of Electrocaloric Effects in Ferroelectric Substances," Status Report No. 3, NASA Research Grant NsG-575 with The University of Kansas, March 1, 1965 to August 31, 1965.
4. G. G. Wiseman et al., "Investigation of Electrocaloric Effects in Ferroelectric Substances," Status Report No. 4, NASA Research Grant NsG-575 with The University of Kansas, September 1, 1965 to February 28, 1966.

5. F. Jona and G. Shirane, "Ferroelectric Crystals," The Macmillan Company, (1962).
6. W. Bantle, "Die spezifische Wärme seignette-elektrischer Substanzen," *Helv. Phys. Acta*, 15, 373-404, (1942).
7. G. Busch, "Neue Seignette-Elektrika," *Helv. Phys. Acta*, 11, 269-298, (1938).
8. C. C. Stephenson and A. C. Zettlemoyer, "The Heat Capacity of KH_2AsO_4 from 15 to 300°K. The Anomaly at the Curie Temperature," *Jour. Am. Chem. Soc.*, 66, 1402-1405, (1944).
9. G. G. Wiseman and J. K. Kuebler, "Electrocaloric Effect in Rochelle Salt," *Phys. Rev.*, 131, 2023-2027, (1963).
10. A. F. Devonshire, "Theory of Ferroelectrics," *Advances in Physics (Phil. Mag. Suppl.)*, 3, 85-130, (1954).
11. W. Kanzig, "Ferroelectrics and Antiferroelectrics," Academic Press, (1957) or F. Seitz and D. Turnbull (Ed.), Solid State Physics, Vol. 4, Academic Press, (1957).